Nonvolatile *alpha*-Branched-Chain Fatty Esters[1]

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Abstract

Nonvolatile *alpha*-branched carboxylic acids and esters have been prepared by a free radical reaction. Various esters of the reaction products of hexadecanoic and octadecanoic acids with the terminal olefins, octene, decene, and dodecene have been synthesized. Fractional crystallization from acetone is a useful method for preparing these compounds in a highly purified state. Mass spectra confirm that branching is found exclusively at the *alpha*- or 2-position.

Introduction

THE PREPARATION of 2-alkyl fatty acids and their esters from the principal component acids of natural fats has been given attention at this laboratory for some time. The stability of these acids and esters, which are branched at the carbon atom *alpha* to the carboxyl group, gives them considerable practical interest. Ault, Micich, et al. (1) synthesized several 2-alkyl fatty acids containing 18–21 carbon atoms. The 2-alkyl acids were synthesized by the di-tertiary butyl peroxide catalyzed addition of linear aliphatic carboxylic acids to the normal terminal olefins in a method originally described by Nikishin, Petrov, and associates (3). The products, obtained in 35–70% yields, were purified by fractional distillation. The surface-active properties of the sodium salts and of their corresponding sulfonated products were measured. Excellent wetting properties were observed for those sulfonated acids in which the hydrophilic portion of the molecule was approximately equidistant from the ends of the hydrocarbon chains.

A later report from this laboratory (2) described a series of methyl esters of 2-alkyl fatty acids containing 28–38 carbon atoms, which were synthesized by the same method. Methods for purifying these high-molecular-weight compounds by chromatographic techniques were investigated. In this way were prepared pure specimens of several α-branched esters with such a high molecular weight that their purification by fractional distillation was hardly feasible. However the chromatographic technique does not lend itself readily to the preparation of larger quantities of the purified products which are essential for evaluation in certain end-uses, such as plasticizers and lubricants.

In this paper is described the method used for the preparation of relatively large quantities (i.e., 100 g or more) of essentially nonvolatile 2-alkyl fatty acids and esters. Properties of the products, which possess a very high degree of purity, are also presented.

Experimental Section

Reagents

Stearic acid used was Hystrene (97%), obtained from the HumKo Products Division, National Dairy Products Corporation. It was found to be quite pure when examined by GLC.

Octene-1 was obtained from the Phillips Petroleum

Company and was 99 mole % pure grade. Decene-1 and dodecene-1 were development chemicals obtained from Gulf Oil; both were reported to be 97.1% pure. All olefins were used without further purification. Di-tertiary butyl peroxide was obtained from the Monomer-Polymer Corporation, Philadelphia, Pa., and used as received.

Esterification

Although all of the starting esters were prepared by conventional techniques, no single procedure was applicable to all of them. Methyl stearate was prepared in the usual way by refluxing the mixture of stearic acid, excess absolute methanol, and catalyst (p-toluenesulfonic acid) overnight (16 hr). The product was recrystallized twice from acetone (10:1). It was quite pure (mp 38.1–38.9C). Benzyl stearate and 2-ethylhexyl stearate were prepared by refluxing the mixture of acid, alcohol, and catalyst in toluene solution by using a modified Dean-Stark type distilling receiver to remove the azeotropically entrained water. Purification of the two esters was carried out by crystallization as described above. Neopentyl stearate was prepared by reacting stearoyl chloride with neopentyl alcohol in pyridine solution. The neopentyl alcohol was dissolved in pyridine, and the stearoyl chloride was added dropwise with rapid stirring. After the addition of the acid chloride the stirring was continued for an additional six hours. The mixture was acidified and the neopentyl ester
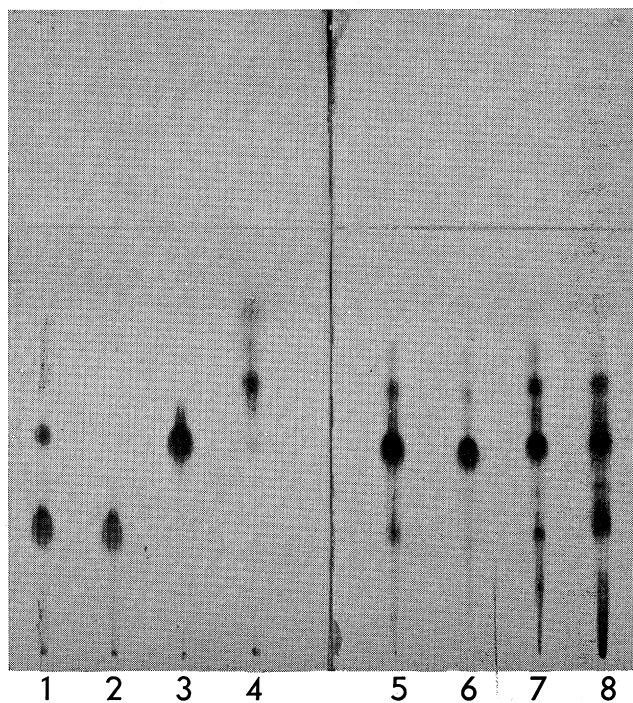

FIG. 1. 1—Crude methyl 2-dodecyloctadecanoate. 2—Unreacted methyl stearate isolated by TLC. 3—Methyl 2-dodecyloctadecanoate purified by TLC. 4—By-products isolated by TLC. 5—Crude methyl 2-dodecyloctadecanoate after removal of methyl stearate by vacuum distillation. 6—Methyl 2-dodecyloctadecanoate purified by crystallization. 7—Precipitate from mother liquors. 8—Residue from mother liquors.

TABLE I
Esters of Branched-Chain Acids. Yield and Properties

Sample	Yield[a] %	M.P. °C	N$_D^{60}$	Molecular Wt. Calc.[b]	Found	C% Calc.	Found	H% Calc.	Found
Methyl stearate		38	1.4241	298					
Methyl 2-octyl-octadecanoate	35	28	1.4372	410	432	78.96	79.10	13.25	13.07
Methyl 2-decyl-octadecanoate	54	37	1.4390	438	438[c]	79.38	79.35	13.32	13.21
Methyl 2-dodecyl-octadecanoate	52	39	1.4412	466	466[c]	79.76	79.65	13.39	13.61
Methyl 2-hexadecyl-[d] octadecanoate		53	1.4470						
Isopropyl-2-decyl-octadecanoate	59	29	1.4375	466	457	79.76	80.41	13.39	13.39
Isobutyl 2-decyl-octadecanoate	52	27	1.4382	480	480[c]	79.93	79.93	13.42	13.25
2-Ethylhexyl 2-decyl-octadecanoate		12	1.4408	536	549	80.52	80.69	13.52	13.52
Neopentyl 2-decyl-octadecanoate	53	22	1.4375	494	494[c]	80.09	80.43	13.44	13.39
Benzyl 2-decyl-octadecanoate		27	1.4612	514	514[c]	81.65	81.71	12.14	12.08
2-Ethylhexyl 2-octyl-octadecanoate		7	1.4403	508	521	80.24	80.41	13.47	13.47
2-Ethylhexyl 2-dodecyl-octadecanoate	51	13	1.4420	564	571	80.78	80.83	13.56	13.59
Isopropyl 2-dodecyl-octadecanoate	56	33.5	1.4387	494	494[c]	80.09	80.23	13.44	13.64
Isobutyl 2-dodecyl-octadecanoate	51	23	1.4401	508	508[c]	80.24	80.30	13.47	13.41

[a] Yield calculated from TLC results; where no yield is shown, ester interchange method was used in preparation.
[b] Calculated values are on basis of carbon = 12, hydrogen = 1, and oxygen = 16.
[c] Molecular weight determined by mass spectrometer; otherwise an isothermal distillation method was used.
[d] Reference 2.

extracted with Skelly B. Purification of the ester was effected chromatographically by using a Florisil column.

Addition of Ester to Olefin

The addition of ester to olefin was carried out as previously described (2). After completing the addition reaction, a sample of the reaction mixture was examined by thin-layer chromatography, and the yield of branched ester was calculated from a TLC prep plate. Vacuum fractional distillation was used to remove the excess of unreacted ester and relatively low boiling byproducts from the reaction mixture. This was accomplished at a distillation temperature of 130–135C at 0.2-mm pressure. The product was obtained from the residual fraction by low-temperature fractional crystallization from acetone. Temperatures used were in the range of −30C to 0C, depending upon the specific compound being prepared. Generally the ratio of solvent to product was 15:1. A recrystallization was essential to obtain analytically pure products in each case. The entire purification process was monitored by thin-layer chromatography.
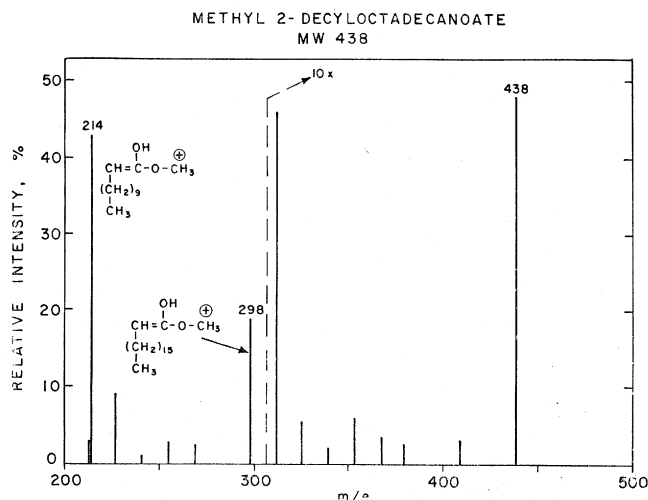
METHYL 2-DECYLOCTADECANOATE
MW 438

FIG. 2. Mass spectrum.

This is illustrated in Figure 1, which shows the characteristic thin-layer chromatographic data which were obtained.

In the preparation of the 2-ethylhexyl and benzyl esters of the α-branched acids, alcoholysis of the corresponding methyl ester was used. To accomplish this, the ester was heated on a steam bath for four hours with an excess of the alcohol by using an alkoxide catalyst. A 1% catalyst ($NaOCH_3$) concentration, based on the weight of ester, was employed, and the weight ratio of alcohol to ester was 5:1. Analytical data pertaining to the compounds prepared are shown in Table I.

Discussion

The yield data shown in Table I refer to calculated yield rather than to the actual isolated yield of the highly purified product. The analytical data have been obtained on the products which were purified by crystallization. In some instances the products were examined by GLC, and a purity of 96–98% was indicated. The high purity of these products is attested by the data from mass spectrometric analysis. Percentage figures for C and H analysis further attest to the purity of these products.
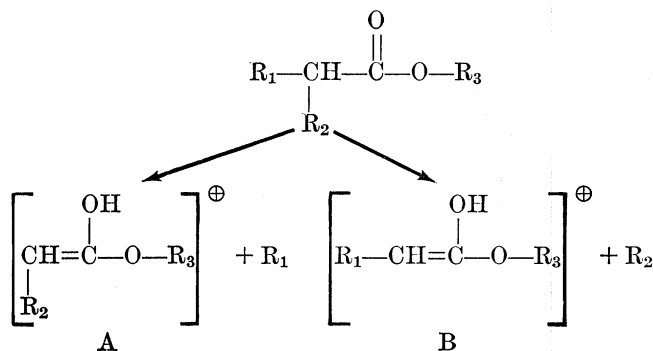
Data in Table I indicate that the introduction of a branch at the α-position lowers the melting point below that of the original ester, provided the normal branch has 10 carbons or less. The effect of increasing the length of the branch is to increase the melting point; if the branch is normal and has 12 carbons or more, it is higher than that of the original ester. Increasing the length of a branch increases the refractive index.

TABLE II
Principal Peaks in Mass Spectra

Compound	Parent peak m/e	A PP-R₁ m/e	B PP-R₂ m/e
Methyl 2-decyloctadecanoate	438	214	298
Methyl 2-dodecyloctadecanoate	466	242	298
i-Butyl 2-decyloctadecanoate	480	256	340
i-Propyl 2-dodecyloctadecanoate	494	270	326
i-Butyl 2-dodecyloctadecanoate	508	284	340

Branching in the alcohol also serves to lower the melting point when compared with that of the corresponding methyl ester. Lowest-melting products are those with a branch in both the acid and alcohol moieties of the esters.

The mass spectra for these compounds show the expected patterns for esters of carboxylic acids branched only in the α-position. For branched esters of this type, fragmentation will occur at the tertiary carbon according to the following scheme (4).

$$
\begin{array}{c}
\overset{\displaystyle O}{\overset{\displaystyle \|}{R_1\!-\!CH\!-\!C\!-\!O\!-\!R_3}} \\
|\\
R_2
\end{array}
$$

$$
\left[\begin{array}{c}OH\\|\\CH\!=\!C\!-\!O\!-\!R_3\\|\\R_2\end{array}\right]^{\oplus} + R_1 \qquad \left[\begin{array}{c}OH\\|\\R_1\!-\!CH\!=\!C\!-\!O\!-\!R_3\end{array}\right]^{\oplus} + R_2
$$

A   B

Of course, fragmentation at other points also occurs to a lesser extent. Significant portions of the mass spectral curve for methyl 2-decyloctadecanoate are shown in Figure 2. The C_{13} isotope peaks $m/e + 1$ have been omitted for simplicity of presentation. The mass spectra of the several compounds investigated follow this expected scheme of fragmentation, as shown in Table II.

Complete spectral data preclude the presence of more than very minor amounts of materials branched at any position on the fatty acid backbone except the *alpha*. This conclusion is in agreement with results reported previously from this laboratory (2).

REFERENCES

1. Ault, W. C., T. J. Micich, A. J. Stirton and R. G. Bistline Jr., JAOCS *42*, 233 (1965).
2. Maerker, G., H. E. Kenney, A. Bilyk and W. C. Ault, Ibid. *43*, 104 (1966).
3. Petrov, A. D., et al., Doklady Akad. Nauk USSR *131*, 580 (1960); Nikishin, G. I., et al., Izv. Akad. Nauk USSR Otd. Khim Nauk, 1326 (1961); Nikishin, G. I., et al., Ibid. 1487 (1961).
4. Ryhage, R., and E. Stenhagen, in "Mass Spectrometry of Organic Ions," ed., F. W. McLafferty, Academic Press Inc., New York, N. Y., 1963, p. 399–452.